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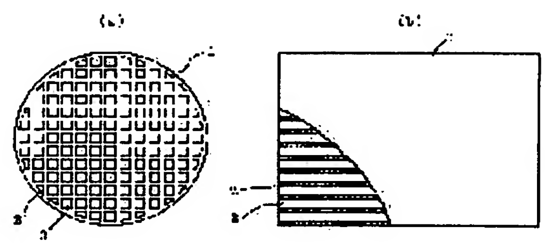
(54) **CERAMIC HONEYCOMB FILTER**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a ceramic honeycomb filter for scavenging of exhaust particulates of a diesel engine of low pressure loss, high scavenging efficiency and high durability.

SOLUTION: This ceramic honeycomb filter constitutes its characteristic feature that a porous bulkhead of a ceramic honeycomb structural body 1 has more than 60% porosity and a more than 15 μm average pore diameter and that the maximum value of Sn expressed under an expression (1) concerning inclination of an accumulated pore capacity distribution curve of the porous bulkhead 2 (curve expressed with a graph with a lateral axis as the pore diameter and a vertical axis as accumulated pore capacity) namely Sn=-(Vn-Vn-1)/(log(Dn)-log(Dn-1)) (1), (where, Dn is a pore diameter (μm) at a No.(n) measuring point, Dn-1 is a pore diameter (μm) at a No.(n-1) measuring point, Vn is accumulated pore capacity (cm3/g) at the number (n) measuring point, Vn-1 is accumulated pore capacity (cm3/g) at the No.(n-1) measuring point and Sn is inclination of the accumulated pore capacity distribution curve against the pore diameter at the No.(n) measuring point).



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CLAIMS

[Claim(s)]
[Claim 1] By carrying out eye closure of the predetermined passage edge of a ceramic honeycomb structure object, and making the septum of the porosity which divides this passage pass exhaust gas In the ceramic honeycomb filter from which the particle contained in exhaust gas is removed When it measures with a method of mercury penetration, said porosity septum 60% or more of porosity, It has the average pole diameter of 15 micrometers or more, the maximum of inclination Sn of the accumulation pore volume distribution curve of said septum to the pole diameter in the n-th point of measurement is 0.7 or more, and inclination Sn of said accumulation pore volume distribution curve is the following formula (1).
Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1), (However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1), Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, and Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1). The ceramic honeycomb filter characterized by what is expressed.
[Claim 2] The ceramic honeycomb filter given in claim 1 term characterized by the maximum of inclination Sn in the accumulation pore volume-of-distribution curve of said porosity septum being 0.9 or more.
[Claim 3] The ceramic honeycomb filter according to claim 1 to 2 characterized by the porosity of said porosity septum being 60 - 80%.
[Claim 4] The ceramic honeycomb filter according to claim 1 to 3 characterized by the average pole diameter of said porosity septum being 15-40 micrometers.
[Claim 5] The ceramic honeycomb filter according to claim 1 to 4 with which chemical composition of the principal component of the porous ceramics which constitute said porosity septum is characterized by the principal component of a crystal phase being cordierite by 2:42 to SiO56 mass %, 2O3:30 to aluminum45 mass %, and MgO:12 - 16 mass %.
[Claim 6] By carrying out eye closure of the predetermined passage edge of a ceramic honeycomb structure object, and making the septum of the porosity which divides this passage pass exhaust gas In the ceramic honeycomb filter with which it is the ceramic honeycomb filter from which the particle contained in exhaust gas is removed, and the catalyst is supported inside said porosity septum front face and the porosity septum When it measures with a method of mercury penetration, said porosity septum 60% or more of porosity, It has the average pole diameter of 15 micrometers or more, the maximum of inclination Sn of the accumulation pore volume distribution curve of said septum to the pole diameter in the n-th point of measurement is 0.7 or more, and inclination Sn of said accumulation pore volume distribution curve is the following formula (1).
Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1), (However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1), Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, and Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1). The ceramic honeycomb filter characterized by what is expressed.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the ceramic honeycomb filter for removing the particle contained in a Diesel engine's emission gas.
[0002]
[Description of the Prior Art] In order to remove the particle discharged by the Diesel engine, the septum of a ceramic honeycomb structure object is made into porous structure, and examination which adopts the filter for particle uptake of the structure of making the exhaust gas which contained the particle in the septum pass (diesel particulate filter) is advanced. About the property of this filter, it is supposed that the collection efficiency of a particle, pressure loss (pressure loss), and three uptake time amount (time amount until it reaches a fixed pressure loss from uptake initiation) of a particle are important. Although uptake time amount will be made for a long time if a pressure loss will increase, uptake time amount will become short, if collection efficiency and a pressure loss have an opposite relation and it is going to make collection efficiency high especially, and a pressure loss is made low, collection efficiency worsens. To a ceramic honeycomb structure object, the technique which controls as follows the magnitude of the pore which exists in porosity, an average pole diameter, and a septum front face has been examined from the former so that the property of these opposite filters may be satisfied.
[0003] While collection efficiency is maintainable from the first stage to a high value by constituting the pore which exists in a filter septum front face from a stoma of 5-40 micrometers of apertures, and an osculum of 40-100 micrometers of apertures, and constituting it from JP,3-10365,B so that the number of these stomata may be 5 to 40 times the number of these osculums, it is indicated that the low exhaust gas clarifying filter of pressure loss is obtained. On the other hand, the average aperture of the internal pore which exists in the interior of a septum is larger than 15 micrometers, and, as for accumulation pore volume, 0.3-0.7cm3/g has become the desirable range. Here, although there is no publication of the porosity P of a septum (volume %), if true specific gravity rho of the cordierite ingredient indicated by the example is made into 2.5 g/cm3, it is computable in the following formulas from the accumulation pore volume V (cm3/g). P=100xVxrho/(1+ Vxrho). Therefore, if range of 0.3-0.7cm 3/g with the desirable accumulation pore volume of the internal pore which exists in the interior of a septum is converted into porosity, it will become 42.8 - 63.6 volume %. (Patent reference 1 reference.)
Moreover, it is indicated by JP,61-54750,B by controlling opening porosity (porosity) and an average pole diameter that the filter from a high collection efficiency type to a low collection efficiency type can be designed. The opening porosity (porosity) and the average pore diameter (average pole diameter) in the band limited as a suitable example in this official report in the boundary to which the point 1-5-6-4 of page [20th] drawing 8 is connected are indicated. For a point 1, opening porosity 58.5 capacity %, the average pore diameter of 1 micrometer, and a point 5 are [opening porosity 62.0 capacity % the average pore diameter of 15 micrometers, and the point 4 of opening porosity 39.5 capacity %, the average pore diameter of 15 micrometers, and a point 6] 1 micrometer in opening porosity 90.0 capacity % and average pore diameter here. (Patent reference 2 reference.)
And it is indicated by JP,9-77573,A by 55 - 80% of porosity and an average pole diameter being 25-40 micrometers, and the pore on the front face of a septum consisting of a 5-40 micrometers stoma and a 40-100-micrometer osculum, and making the number of these stomata into five to 40 times of the number of these osculums that the honeycomb structure object which doubles and has the property of high collection efficiency, low voltage loss, and low coefficient of thermal expansion is acquired. (Patent reference 3 reference.)
[0004]
[Patent reference 1] JP,3-10365,B [the patent reference 2] JP,61-54750,B (drawing 8)
[Patent reference 3] JP,9-77573,A [0005]
[Problem(s) to be Solved by the Invention] However, as shown in the above-mentioned Prior art, although the balance of porosity and collection efficiency can be attained to some extent, by optimization of the magnitude of the hole on porosity, an average pole diameter, and the front face of a septum, the septum itself is a porous body, and since the reinforcement of a porous body has the relation which disagrees with the porosity and an average pole diameter, the reinforcement of a ceramic honeycomb structure object will fall inevitably. That is, if porosity and the magnitude of pore become large, the reinforcement of a ceramic honeycomb structure object will fall. In order to obtain the filter of low voltage force loss, especially when it makes porosity 60% or more and an average pole diameter is set to 15 micrometers or more, lowering on the strength becomes remarkable. For this reason, without damaging with the thermal stress generated when low voltage force loss and high collection efficiency are reconciled and it is moreover used as a Diesel engine's filter for particle uptake, thermal shock stress, the mechanical bolting force at the time of assembly, the stress by oscillation, etc., there is a problem that the ceramic honeycomb filter which has rear-spring-supporter endurance in a long period of time is not obtained, and it had become the failure of utilization of a diesel particulate filter.
[0006] this invention aim at offer the ceramic honeycomb filter which have rear spring supporter endurance to a long period of time, without damage with the thermal stress which generate it when the porosity of a septum be use as a Diesel engine filter for particle uptake also as an average pole diameter of 15 micrometers or more 60% or more, thermal shock stress, the mechanical bolting force at the time of assembly, the stress by oscillation, etc. so that the filter of low voltage force loss may be obtain in order to solve the above-mentioned problem.
[0007]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention person hit on an idea of low voltage force loss, high collection efficiency, and the ceramic honeycomb filter to which the three properties of high intensity were satisfied further being obtained to a header and this invention by making into a certain fixed within the limits distribution of the pore formed in the septum of a honeycomb structure object, as a result of inquiring wholeheartedly. That is, it be the following formula (1)

concern [when said porosity septum be measure with a method of mercury penetration in the ceramic honeycomb filter from which the particle contain in exhaust gas be remove, have 60% or more of porosity, and the average pole diameter of 15 micrometers or more, and] the inclination of the accumulation pore volume distribution curve of said porosity septum by the ceramic honeycomb filter of this invention carry out eye closure of the predetermined passage edge of a ceramic honeycomb structure object, and make the septum of the porosity which divide this passage pass exhaust gas.
Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1), (However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1). Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1), and Sn is the inclination of the accumulation pore volume distribution curve over the pole diameter in the n-th point of measurement. It is characterized by the maximum of Sn expressed being 0.7 or more. At this time, as for the maximum of Sn, it is desirable that it is 0.9 or more, and it is suitable that porosity is 60 - 80% and an average pole diameter is 15-40 micrometers. Furthermore, the chemical composition of the principal component of the porous ceramics which constitute a septum is 2:42 to SiO56 mass %, 2O3:30 to aluminum45 mass %, and 12 to MgO:16 mass %, and it is suitable that the principal component of a crystal phase is cordierite. Moreover, the ceramic honeycomb filter of this invention By carrying out eye closure of the predetermined passage edge of a ceramic honeycomb structure object, and making the septum of the porosity which divides this passage pass exhaust gas In the ceramic honeycomb filter with which it is the ceramic honeycomb filter from which the particle contained in exhaust gas is removed, and the catalyst is supported inside said porosity septum front face and the porosity septum Said porosity septum is the following formula (1) concerning [when it measures with a method of mercury penetration, have 60% or more of porosity, and the average pole diameter of 15 micrometers or more, and] the inclination of the accumulation pore volume distribution curve of said porosity septum.
Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1), (However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1). Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1), and Sn is the inclination of the accumulation pore volume distribution curve over the pole diameter in the n-th point of measurement. It is characterized by the maximum of Sn expressed being 0.7 or more.

[0008]

[Function] Next, it explains per [in this invention] operation effectiveness. With the ceramic honeycomb filter of this invention, the porosity septum of a ceramic honeycomb structure object is the following formula (1) concerning [when it measures with a method of mercury penetration, have 60% or more of porosity, and the average pole diameter of 15 micrometers or more, and] the inclination of the accumulation pore volume distribution curve (curve expressed with the graph which makes an axis of abscissa a pole diameter and makes an axis of ordinate accumulation pore volume) of said porosity septum.
Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1), (However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1). Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1), and Sn is the inclination of the accumulation pore volume distribution curve over the pole diameter in the n-th point of measurement. Since the maximum of Sn expressed is 0.7 or more, pore distribution becomes sharp with high porosity, and since the rate that the pore centering on an average pole diameter occupies increases, while pressure loss is suppressed low, it becomes possible to maintain reinforcement highly. Here, the reason which limited inclination Sn of an accumulation pore volume distribution curve is explained to a detail. Although the reinforcement of a ceramic honeycomb structure object of being influenced of porosity or an average pole diameter is natural, it is large that it is dependent on pore volume distribution, and if especially pore volume distribution is put in another way as Sharp, even if porosity is 15 micrometers or more in average pole diameter, it will depend on having found out that high intensity was obtained 60% or more by raising the homogeneity of a pore dimension. Inclination Sn of porosity, an average pole diameter, and an accumulation pore volume distribution curve used the auto pore III9410 made from Micromeritics, and measured it with the method of mercury penetration here. In measurement of this method of mercury penetration, after containing the sample for measurement in a measurement cel and decompressing the inside of a cel, mercury is introduced and pressurized and it asks for the relation between a pole diameter and accumulation pore volume from the relation between the pressure at this time, and the volume of the mercury pushed in into the pore which exists in a sample. That is, if welding pressure is large, mercury will infiltrate even into more detailed pore and the volume of the detailed pore equivalent to welding pressure will be measured. For this reason, measurement is performed one by one to a small thing from what has a large pole diameter. At this time, that for which it asked by the above-mentioned formula (1) serves as inclination Sn in the point of measurement of eye (n) watch from the pole diameter Dn in point of measurement and the accumulation pore volume Vn of eye the watch [pole diameter Dn-1 in the point of measurement of eye watch (n-1) and accumulation pore volume Vn-1 and (n) watch] from measurement initiation. An example of the measurement result of Sn is shown in drawing 3 . It is the inclination S1 [(V1-V2) /(logD1-logD2)] for which it asked from pole diameters D1 and D2 and the accumulation pore volume V1 and V2. [in / on drawing 3 and / in Point a / the 1st and the 2nd point of measurement] Point b is the inclination S2 [(V2-V3) /(logD2-logD3)] for which it asked from the pole diameters D2 and D3 and the accumulation pore volume V2 and V3 in the 2nd and the 3rd point of measurement. Here, pore volume distribution is broadcloth as the maximum of Sn is less than 0.7, and distribution of inclination Sn of the pole diameter shown in drawing 3 and an accumulation pore volume distribution curve shows that pore volume distribution is dramatically sharp in if the maximum of Sn is 0.7 or more. If the rate of the big and rough pore which caused the lowering on the strength by pore volume distribution being broadcloth, and the detailed pore from which a particle carries out blinding and causes pressure-loss buildup falls and the maximum of Sn becomes [** with difficult coexistence of low voltage loss and high intensity] 0.7 or more, since pore volume distribution will become Sharp, the rate of big and rough pore or detailed pore falls, and coexistence of low voltage loss and high intensity can be attained. This is clear also from drawing 4 which shows the maximum of inclination Sn of an accumulation pore volume distribution curve, and the relation of A axial compression intensity ratio. Here, A axial compression intensity ratio is the relative value of A axial compression reinforcement which asked for elegance level as 1.0 conventionally. When the maximum of Sn becomes 0.7 or more, it turns out that A axial compression reinforcement becomes 1.5 or more [of elegance level (the maximum of Sn is 0.6 or less field)] conventionally. That is, when the maximum of Sn becomes 0.7 or more, it turns out that the mechanical strength of a ceramic honeycomb structure object improves remarkably. In order to reconcile low voltage force loss and high intensity, as for the maximum of Sn, 0.9 or more are more desirable. Here, the porosity of limiting the porosity of a ceramic honeycomb structure object to 60% or more is because the pressure loss of a filter becomes high at less than 60%. Moreover, if porosity exceeds 80%, while the reinforcement of a filter will fall, since the collection efficiency of a particle also worsens, it is the range where 60 - 80% of porosity is desirable. Furthermore, the effectiveness of being 65% or more of porosity, and reducing pressure loss becomes still larger, and it is 75% or less of porosity, and since decline in reinforcement or collection efficiency can be made smaller, it is the range where 65 - 75% of porosity is more desirable. Moreover, an average pole diameter is because, as for limiting the average pole diameter of the pore which exists in the ceramic honeycomb

structure to 15 micrometers or more, the pressure loss of a filter becomes large by less than 15 micrometers. Moreover, when an average pole diameter exceeds 40 micrometers, while the reinforcement of a filter falls, since a filter is passed without catching a small particle and collection efficiency worsens, it is the range where the average pole diameter of 15-40 micrometers is desirable. Furthermore, it is 25 micrometers or less in average pole diameter, and since decline in reinforcement or collection efficiency can be made smaller, it is the desirable range rather than it can attain coexistence of the property that high intensity disagrees [the average pole diameter of 15-25 micrometers] with low voltage force loss.

[0009] In the ceramic honeycomb filter of this invention, the chemical composition of the principal component of the porous ceramics which constitute the septum of a honeycomb structure object And 2:42 to SiO56 mass %, Having presupposed that it is suitable that the principal component of a crystal phase is cordierite at 2O3:30 to aluminum45 mass % and MgO:12 - 16 mass % Although it is because the ceramic honeycomb filter which a crack cannot generate easily is obtained even if it uses the low thermal expansion nature which cordierite has originally and a thermal shock is added This invention is not limited to this and can use ingredients, such as other heat-resistant ceramics, for example, a mullite, an alumina, silicon nitride, silicon carbide, nitriding aluminum, lithium aluminium silicate, aluminum titanate, and a zirconia.

[0010] Moreover, it is the following formula (1) concerning [when the porosity septum of a ceramic honeycomb structure object is measured with a method of mercury penetration in the ceramic honeycomb filter with which the catalyst is supported inside the porosity septum front face and the porosity septum, have 60% or more of porosity, and the average pole diameter of 15 micrometers or more, and] the inclination of the accumulation pore volume distribution curve (curve expressed with the graph which makes an axis of abscissa a pole diameter and makes an axis of ordinate accumulation pore volume) of said porosity septum.

Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1), (However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1). Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1), and Sn is the inclination of the accumulation pore volume distribution curve over the pole diameter in the n-th point of measurement. It is because the effectiveness of reconciling low voltage force loss which was mentioned above, high collection efficiency, and high intensity from the maximum of Sn expressed being 0.7 or more is remarkable in the interior of a septum front face and a septum in the ceramic honeycomb filter with which the catalyst is supported.

[0011] The ceramic honeycomb structure object of this invention can be manufactured as follows. The porosity after first calcinating the ostomy material to which especially the particle size of 20-100 micrometers occupies 50% or more the mean particle diameter of 20 micrometers or more to ceramic raw material powder adds in the range obtained 60 to 80%. Shaping assistants, such as a binder and lubricant, are added if needed to this mixture, water is added and the batch which can be plasticized is produced, after mixing. After carrying out extrusion molding of the Plastic solid of honeycomb structure for this batch by the well-known extrusion method, the honeycomb structure object which has the pore formed into the septum of the trace after the micropore of a ceramic proper and ostomy material combustion clearance is acquired by performing desiccation, combustion clearance of ostomy material, and baking. Thus, maximum of Sn which shows the sharpness of pore distribution with the ability of the average pole diameter of a septum to be stored in the range of 15-25 micrometers with combination with the pore formed of the ostomy material (the particle size of 20-100 micrometers occupies 50% or more with the mean particle diameter of 20 micrometers or more) to which the micropore which the ceramics holds originally, and particle size were equal can be made or more into 0.7. Since especially the nature ceramics of cordierite has pore with a pole diameter of about 1-20 micrometers originally, it is 20 micrometers or more in mean particle diameter, and its combination with the ostomy material to which the particle size of 20-100 micrometers occupies 50% or more is effective. In addition, ostomy material is well-known graphite, wheat flour, resin powder, etc., and it is desirable to classify so that the mean particle diameter of 20 micrometers or more and the particle size of 20-100 micrometers may serve as particle size distribution which occupy 50% or more. Moreover, when using resin powder, it is good also as particle size distribution to which the manufacture condition is adjusted and the mean particle diameter of 20 micrometers or more and the particle size of 20-100 micrometers occupy 50% or more. moreover, ostomy material -- abbreviation -- the pore formed into a septum as it is spherical -- abbreviation -- since it becomes spherical, it is desirable from the ceramic honeycomb structure object which has the mechanical strength which could reduce the stress concentration to pore and was excellent being acquired. Furthermore, it is desirable from becoming possible to remove out of a septum easily, in case combustion clearance of the ostomy material is carried out to ostomy material being hollow, the problem that a crack goes into a septum being unable to arise easily, in case it is combustion clearance, and the manufacture yield improving.

[0012]

[Embodiment of the Invention] Although the actual example of this invention is explained hereafter, this invention is not limited to them.

(Example 1) SiO2 carried out specified quantity mixing of three kinds of spherical resin powder of No.1-3 as a binder, lubricant, and ostomy material at cordierite-ized ceramic raw material powder, such as a kaolin, a temporary-quenching kaolin, an alumina, an aluminum hydroxide, a silica, and talc, respectively so that 42 to 56 mass % and aluminum 2O3 might become 30 to 45 mass % and MgO might become 12 - 16 mass %. At this time, the particle size distribution of the spherical resin powder used as ostomy material are shown in drawing 5 , and a rate with a mean particle diameter and a particle size of 20-100 micrometers is shown in a table 1. Next, water was added into this mixture, the batch which can be plasticized was produced, and the cylindrical shape honeycomb structure object was fabricated for this batch by the well-known extrusion method. subsequently, after drying this Plastic solid, it calcinates in a 1380-1420-degree C temperature region, and it is shown in the front view and side elevation of drawing 1 (a) and (b) -- as -- from the porosity ceramic septum 3 and a breakthrough 2 -- becoming -- ostomy material -- three kinds of nature of cordierite ceramic honeycomb structure objects 1 of trial No.1-3 corresponding to No.1-3 were acquired. The diameter of the acquired honeycomb structure object was 152mm in 143mm and die length, and the number of the wall thickness of a septum was [the number of the passage per two] 46 1cm 0.3mm.

[0013] The auto pore III9410 made from Micromeritics was used, and inclination Sn of the porosity of three kinds of nature of cordierite ceramic honeycomb structure objects of obtained trial No.1-3, an average pole diameter, and an accumulation pore volume distribution curve was measured with the method of mercury penetration. Although the numeric values acquired by measurement were the pressure of the mercury added to the sample, and the volume of the mercury pressed fit into the sample, the pole diameter Dn of the point of measurement of eye (n) watch was calculated from (2) types, and the accumulation pore volume Vn of the point of measurement of eye (n) watch was calculated from (3) types.

(n) Pole diameter Dn=-4alphacos theta/Pn of the point of measurement of eye watch (2)

Here, alpha is the surface tension (4.935x10-4 kg/cm) of mercury.

theta is the contact angle (130 degrees) of mercury and a solid-state.

Pn is the pressure of the mercury of the point of measurement of eye (n) watch.

(n) Accumulation pore volume Vn=vn/w of the point of measurement of eye watch (3)

Here, the volume w of the sample by which vn was pressed fit into the sample of the point of measurement of eye (n) watch is the weight of a sample. The relation (accumulation pore volume distribution curve) of the pole diameter and accumulation pore volume which were obtained is shown in drawing 6 . Although the inclination of the accumulation pore volume distribution curve of the honeycomb structure object of trial No.1 was dramatically steep and the inclination of the accumulation pore volume distribution curve of the honeycomb structure object of trial No.2 was also steep among about 10 micrometers - about 100 micrometers so that clearly from drawing 6 , the inclination of the accumulation pore volume distribution curve of the honeycomb structure object of trial No.3 was comparatively loose. From the accumulation pore volume distribution curve shown in the above and drawing 6 , inclination Sn of the accumulation pore volume distribution curve of the honeycomb structure object of trial No.1-3 was calculated. Although inclination Sn of an accumulation pore volume distribution curve asks for a smooth approximation curve from the plot of measurement data and should just be going to ask for it on the curve as a differential value in minute spacing of a pole diameter Since the accumulation pore distribution curve is fully smooth and point of measurement is regular intervals substantially about the logarithm (logDn) of a pole diameter, so that clearly from drawing 6 (n) Even if it calculates inclination Sn from the measured value of the pole diameter in the point of measurement of eye watch, and the point of measurement of eye watch (n-1), and accumulation pore volume, it is almost without error. Thus, the pole diameter of each honeycomb structure object and the relation of inclination Sn of an accumulation pore volume distribution curve which were obtained are shown in drawing 7 . Sn of the honeycomb structure object of trial No.1 which was the steepest was the highest at the accumulation pore volume distribution curve of drawing 6 , Sn of the next steep honeycomb structure object of trial No.2 was next high, and Sn of the honeycomb structure object of trial No.3 which was comparatively loose was the smallest. Thus, the measurement result of the maximum of calculated Sn and porosity, and an average pole diameter was indicated to a table 2.
[0014]
[A table 1]

造孔材	平均粒径 (μm)	20–100μmの粒径の割合 (質量%)
No.1	64	75
No.2	62	62
No.3	52	48

[0015] The end face of the ceramic honeycomb structure object produced as mentioned above was stopped as the front view and side elevation were shown in drawing 2 (a) and (b), and it ******(ed) by ** 5, and the porosity ceramic honeycomb filter was obtained. The filter shape of this obtained porosity ceramic honeycomb filter was evaluated about a pressure loss and breakage-proof nature. The result is doubled and it is shown in a table 2. When it was the pressure loss below the value permitted practical, it considered as acceptance, the pressure loss honeycomb filter inflow before when a pressure loss passes the air of a predetermined flow rate here in a pressure loss test stand, and after runoff estimated, when it was (O) and was the pressure loss exceeding the pressure loss permitted practical, it considered as the rejection, and (x) showed. The value of A axial compression intensity ratio estimated breakage-proof nature, this set elegance level to 1.0 conventionally, the case of 1.5 or more was considered as acceptance, it is (O), and it is (O) and (x) showed [in further 2.0 or more desirable cases, it was made into the rejection at the case of less than 1.5 and] them. moreover, the specification M as which Society of Automotive Engineers of Japan determines measurement of A axial compression reinforcement -- it carried out according to 505-87 "the test method of the ceramic monolith support for automobile exhaust air gas cleanup catalysts." And when both a pressure loss and breakage-proof nature had (O), among those the (O) judging as a comprehensive judgment in some which are acceptance, (x) estimated (O) and the thing whose at least one is a rejection.
[0016]
[A table 2]

試験No		隔壁の材料特性			フィルター特性		総合判定
		気孔率 (%)	平均細孔径 (μm)	累積細孔容積分布曲線の傾きSnの最大値	圧力損失	耐破損性	
試験No.1	本発明例	65.0	20.8	1.12	○	◎	◎
試験No.2		66.4	22.0	0.85	○	○	○
試験No.3	比較例	67.3	19.5	0.66	○	×	×

[0017] In the ceramic honeycomb filter shown in trial No.1-2 which are an example of this invention among the results shown in a table 2, since the maximum of inclination Sn in an accumulation pore volume distribution curve was 0.7 or more, even if porosity was a porous material of 15 micrometers or more in 60% or more and an average pole diameter, pressure loss was low, it passed also about breakage-proof nature, and comprehensive judgments were (O) and (O). Although pressure loss passed since the maximum of inclination Sn [in / in the ceramic honeycomb filter shown in trial No.3 of the example of a comparison on the other hand among the results shown in a table 2 / an accumulation pore volume distribution curve] turned around 0.7 the bottom, breakage-proof nature became rejection (x) and the comprehensive judgment was (x). As mentioned above, when the comprehensive judgment was carried out from the result of the pressure loss which is a property important as a filter for particle uptake, and breakage-proof nature so that clearly from the result of a table 2, each of ceramic honeycomb filters of trial No.1-2 which are the example of this invention was filters with which are satisfied of a pressure-loss property and breakage-proof nature.
[0018] (Example 2) The batch in which the same plasticization as trial No.1 of an example 1 is possible was produced, and the cylindrical shape honeycomb structure object was fabricated for this batch by the well-known extrusion method. Under the present circumstances, the dimension of well-known metal mold was adjusted so that the number of the passage per two might be obtained 1cm in various kinds of septum thickness. Subsequently, after drying this Plastic solid, it calcinated in the 1380-1420-degree C temperature region, and the various nature of cordierite ceramic honeycomb structure objects 1 which consist of a porosity ceramic septum 3 and a breakthrough 2 were acquired. The diameter of the acquired honeycomb structure object was 152mm in 143mm and

die length, and as shown in trial No.4-8, for the wall thickness of a septum, the number of the passage per two was five of 39-62 pieces 1cm 0.15mm - 0.33mm. Hereafter, by the same approach as an example 1, after performing ****** of an end face, measurement about the pressure loss which is a filter shape, and breakage-proof nature was performed. The result is shown in a table 3. In addition, the maximum of inclination Sn [in / porosity / all / of trial No.4-8 / in 65% and an average pole diameter / 20.8% and an accumulation pore volume distribution curve] was 1.12.

[0019]

[A table 3]

試験 No		隔壁構造		フィルター特性		
		壁厚 (mm)	流路の数 (個/cm²)	圧力損失	耐破損性	総合判定
試験 No.4	本発明例	0.15	46	○	○	○
試験 No.5		0.2	46	○	○	○
試験 No.6		0.33	46	○	◎	◎
試験 No.7		0.3	62	○	◎	◎
試験 No.8		0.3	39	○	○	○

[0020] As shown in a table 3, even if the ceramic honeycomb filter shown in trial No.4-8 which are an example of this invention was which bulkhead structure, the comprehensive judgment of a filter shape was (O) or (O).

[0021] (Example 3) The catalyst was supported to a septum front face and the interior as follows to the ceramic honeycomb filter of trial No.1-3 used in the example 1.

[0022] As a high specific-surface-area ingredient, alumina sol was mixed with the activated alumina of 5 micrometers of diameters of a centriole with water, and the wash coat of the filter obtained by the agitated activated-alumina slurry was carried out. Then, the slurry adhering to an excess was removed, coating was repeated, and the filter of amount of coats 60 g/L was produced. After having dipped after baking and into the chloroplatinic acid water solution at 800 degrees C after making it dry at 120 degrees C after that furthermore, and making it dry at 120 degrees C, it calcinated at 800 degrees C and the ceramic honeycomb filter which made platinum support was obtained. The amounts of support of the platinum at this time were about 2 g/L.

[0023] Pressure loss was measured by the same approach as an example 1 to the filter of the ceramic honeycomb filter after this catalyst support. Furthermore, the carbon of the specified quantity is thrown into a predetermined flow rate in a pressure loss test stand. Pressure loss difference deltaP before and behind carbon prehension at the time of making a honeycomb filter catch carbon (pressure loss before the pressure loss-carbon prehension after carbon prehension) is measured. When it was the pressure loss exceeding the value which considers as acceptance and is permitted practical by (O) if pressure loss difference deltaP is below the value permitted practical, it considered as the rejection and (x) showed. A result is doubled and it is shown in a table 4.

[0024]

[A table 4]

試験 No		触媒担持後の圧力損失	触媒担持後 カーボン捕捉試験前後の圧力損失差ΔP
試験 No.1	本発明例	○	○
試験 No.2		○	○
試験 No.3	比較例	×	×

[0025] Most lifting of the pressure loss according [the ceramic honeycomb filter shown in trial No.1-2 which are an example of this invention among the results shown in a table 4] to catalyst support was not accepted, but all the results of pressure loss were passing (O). As for the ceramic honeycomb filter shown in trial No.3 which are an example of a comparison on the other hand, lifting of pressure loss was accepted by catalyst support, and the result of pressure loss became rejection (x). Moreover, the honeycomb filter which shows the ceramic honeycomb filter shown in trial No.1-2 which are an example of this invention to trial No.3 acceptance (O) and whose **** are the examples of a comparison under with the value with which pressure loss difference deltaP before and behind carbon prehension is permitted practical became rejection (x) exceeding the value with which deltaP is permitted practical. As mentioned above, the ceramic honeycomb filter of the filter engine performance in which lifting of pressure loss and pressure loss lifting by carbon prehension were small excellent being shown whose maximum of inclination Sn in an accumulation pore volume distribution curve is 0.7 or more is clear also in after catalyst support.

[0026]

[Effect of the Invention] Even if porosity is 60% or more and an average pole diameter is 15 micrometers or more in high value by making or more into 0.7 maximum of inclination Sn in the accumulation pore volume distribution curve of the pore in the septum of the ceramic honeycomb structure object which constitutes a ceramic honeycomb filter, when it is used as a diesel particulate filter according to this invention, it is possible to reconcile both the opposite properties of low voltage force loss and high collection efficiency that are properties. And the ceramic honeycomb filter excellent in endurance which is not damaged to the thermal stress or thermal shock stress at the time of an activity, and the mechanical bolting force of ****** or the stress by oscillation is obtained.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] (a) And (b) is the front view and side elevation showing an example of a honeycomb structure object, respectively.
[Drawing 2] (a) And (b) is the front view and side elevation showing an example of the filter which used the honeycomb structure object, respectively.
[Drawing 3] It is the graph of an example which shows the relation of the pole diameter and inclination Sn of an accumulation pore volume distribution curve which were calculated with the method of mercury penetration.
[Drawing 4] It is the graph of an example which shows the relation between the maximum of inclination Sn of an accumulation pore volume distribution curve, and A axial compression intensity ratio.
[Drawing 5] It is the graph which shows the particle size distribution of the ostomy material used in the example 1.
[Drawing 6] It is the graph which shows the relation of the pole diameter of the test piece of trial No.1-3 and accumulation pore volume in an example 1.
[Drawing 7] It is the graph which shows the relation of the pole diameter of the test piece of trial No.1-3 and inclination Sn of an accumulation pore volume distribution curve in an example 1.
[Description of Notations]
1: ceramic honeycomb structure object 2: -- septum 3: -- the inclination S1 for which it asked from a breakthrough, a 4:ceramic honeycomb filter, and the 1st [in / it 5: stops and / ** and a:accumulation pore volume distribution curve], and the 2nd measurement result, and inclination S2 for which it asked from the 2nd and the 3rd measurement result in b:accumulation pore volume distribution curve,

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[Translation done.]

* NOTICES *

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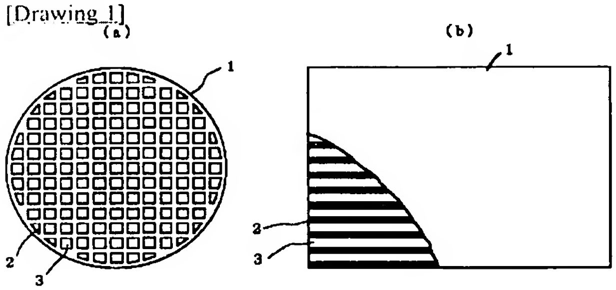
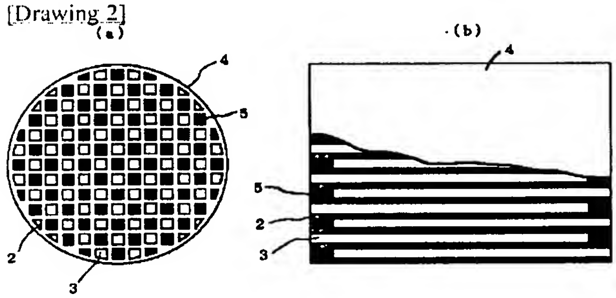
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

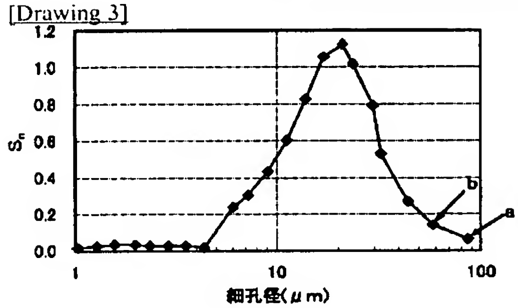
[Drawing 1]



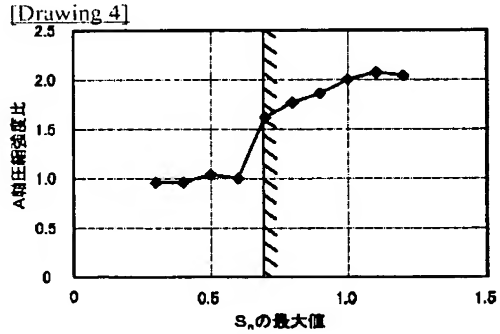
[Drawing 2]



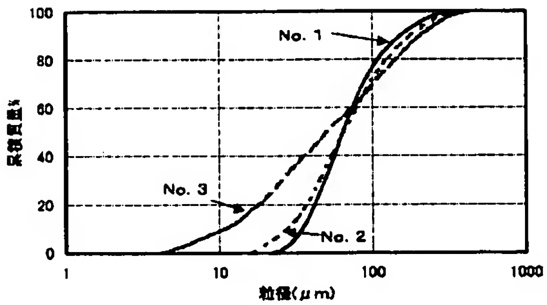
[Drawing 3]



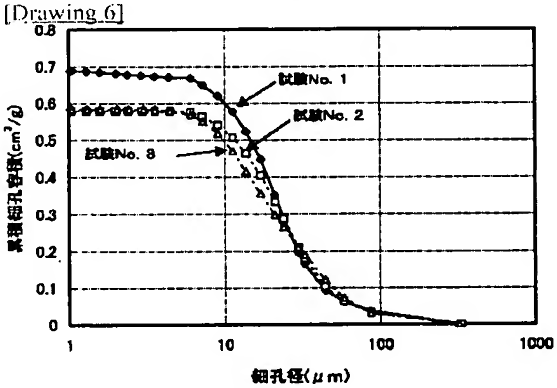
[Drawing 4]



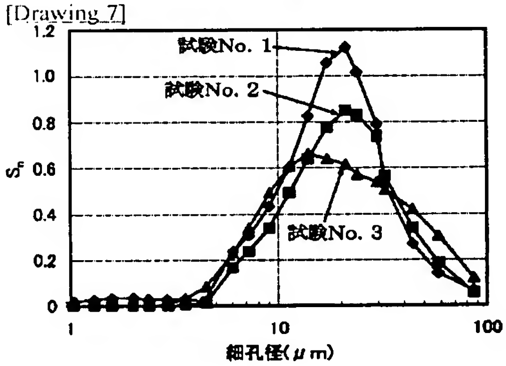
[Drawing 5]



[Drawing 6]



[Drawing 7]



[Translation done.]

WRITTEN AMENDMENT

-- [procedure amendment]
[Filing Date] April 15, Heisei 15 (2003. 4.15)
[Procedure amendment 1]
[Document to be Amended] Description
[Item(s) to be Amended] Claim
[Method of Amendment] Modification
[Proposed Amendment]
[Claim(s)]
[Claim 1] After the mean particle diameter of 20 micrometers or more and the particle size of 20-100 micrometers add at least the ostomy material which has 50% or more of particle size distribution to ceramic raw material powder, By carrying out eye closure of the predetermined passage edge of the ceramic honeycomb structure object which dries the batch which carried out addition mixing of the water etc. after extrusion molding, calcinates, and is acquired, and making the septum of the porosity which divides this passage pass exhaust gas In the ceramic honeycomb filter from which the particle contained in exhaust gas is removed When it measures with a method of mercury penetration, said porosity septum 60% or more of porosity, It has the average pole diameter of 15 micrometers or more, the maximum of inclination Sn of the accumulation pore volume distribution curve of said septum to the pole diameter in the n-th point of measurement is 0.7 or more, and inclination Sn of said accumulation pore volume distribution curve is the following formula (1).
Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1),
(However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1), Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, and Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1). The ceramic honeycomb filter characterized by what is expressed.
[Claim 2] The ceramic honeycomb filter given in claim 1 term characterized by the maximum of inclination Sn in the accumulation pore volume-of-distribution curve of said porosity septum being 0.9 or more.
[Claim 3] The ceramic honeycomb filter according to claim 1 to 2 characterized by the porosity of said porosity septum being 60 - 80%.
[Claim 4] The ceramic honeycomb filter according to claim 1 to 3 characterized by the average pole diameter of said porosity septum being 15-40 micrometers.
[Claim 5] The ceramic honeycomb filter according to claim 1 to 4 with which chemical composition of the principal component of the porous ceramics which constitute said porosity septum is characterized by the principal component of a crystal phase being cordierite by 2:42 to SiO56 mass %, 2O3:30 to aluminum45 mass %, and MgO:12 - 16 mass %.
[Claim 6] After the mean particle diameter of 20 micrometers or more and the particle size of 20-100 micrometers add at least the ostomy material which has 50% or more of particle size distribution to ceramic raw material powder, By carrying out eye closure of the predetermined passage edge of the ceramic honeycomb structure object which dries the batch which carried out addition mixing of the water etc. after extrusion molding, calcinates, and is acquired, and making the septum of the porosity which divides this passage pass exhaust gas In the ceramic honeycomb filter with which it is the ceramic honeycomb filter from which the particle contained in exhaust gas is removed, and the catalyst is supported inside said porosity septum front face and the porosity septum When it measures with a method of mercury penetration, said porosity septum 60% or more of porosity, It has the average pole diameter of 15 micrometers or more, the maximum of inclination Sn of the accumulation pore volume distribution curve of said septum to the pole diameter in the n-th point of measurement is 0.7 or more, and inclination Sn of said accumulation pore volume distribution curve is the following formula (1).
Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1),
(However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1), Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, and Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1). The ceramic honeycomb filter characterized by what is expressed.
[Procedure amendment 2]
[Document to be Amended] Description
[Item(s) to be Amended] 0007
[Method of Amendment] Modification
[Proposed Amendment]
[0007]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention person hit on an idea of low voltage force loss, high collection efficiency, and the ceramic honeycomb filter to which the three properties of high intensity were satisfied further being obtained to a header and this invention by making into a certain fixed within the limits distribution of the pore formed in the septum of a honeycomb structure object, as a result of inquiring wholeheartedly. Namely, the ceramic honeycomb filter of this invention The ostomy material to which the mean particle diameter of 20 micrometers or more and the particle size of 20-100 micrometers have 50% or more of particle size distribution to ceramic raw material powder, By carrying out eye closure of the predetermined passage edge of the ceramic honeycomb structure object which dries the batch which carried out addition mixing of the

water etc. after extrusion molding, calcinates, and is acquired, and making the septum of the porosity which divides this passage pass exhaust gas It is the following formula (1) concerning [when said porosity septum is measured with a method of mercury penetration in the ceramic honeycomb filter from which the particle contained in exhaust gas is removed, have 60% or more of porosity, and the average pole diameter of 15 micrometers or more, and] the inclination of the accumulation pore volume distribution curve of said porosity septum.
Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1),
(However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1). Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1), and Sn is the inclination of the accumulation pore volume distribution curve over the pole diameter in the n-th point of measurement. It is characterized by the maximum of Sn expressed being 0.7 or more. At this time, as for the maximum of Sn, it is desirable that it is 0.9 or more, and it is suitable that porosity is 60 - 80% and an average pole diameter is 15-40 micrometers. Furthermore, the chemical composition of the principal component of the porous ceramics which constitute a septum is 2:42 to SiO56 mass %, 2O3:30 to aluminum45 mass %, and 12 to MgO:16 mass %, and it is suitable that the principal component of a crystal phase is cordierite. Moreover, the ceramic honeycomb filter of this invention The ostomy material to which the mean particle diameter of 20 micrometers or more and the particle size of 20-100 micrometers have 50% or more of particle size distribution to ceramic raw material powder, By carrying out eye closure of the predetermined passage edge of the ceramic honeycomb structure object which dries the batch which carried out addition mixing of the water etc. after extrusion molding, calcinates, and is acquired, and making the septum of the porosity which divides this passage pass exhaust gas In the ceramic honeycomb filter with which it is the ceramic honeycomb filter from which the particle contained in exhaust gas is removed, and the catalyst is supported inside said porosity septum front face and the porosity septum Said porosity septum is the following formula (1) concerning [when it measures with a method of mercury penetration, have 60% or more of porosity, and the average pole diameter of 15 micrometers or more, and] the inclination of the accumulation pore volume distribution curve of said porosity septum.
Sn=-(Vn-Vn -1)/(log(Dn)-log (Dn-1)) (1),
(However, Dn is a pole diameter (micrometer) in the point of measurement of eye (n) watch.) Dn-1 is a pole diameter (micrometer) in the point of measurement of eye watch (n-1). Vn is the accumulation pore volume (cm3/g) in the point of measurement of eye (n) watch, Vn-1 is the accumulation pore volume (cm3/g) in the point of measurement of eye watch (n-1), and Sn is the inclination of the accumulation pore volume distribution curve over the pole diameter in the n-th point of measurement. It is characterized by the maximum of Sn expressed being 0.7 or more.

[Translation done.]

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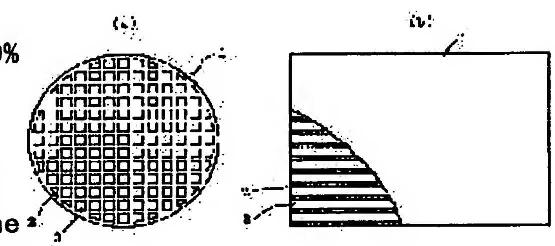
(54) CERAMIC HONEYCOMB FILTER

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a ceramic honeycomb filter for scavenging of exhaust particulates of a diesel engine of low pressure loss, high scavenging efficiency and high durability.
SOLUTION: This ceramic honeycomb filter constitutes its characteristic feature that a porous bulkhead of a ceramic honeycomb structural body 1 has more than 60% porosity and a more than 15 μm average pore diameter and that the maximum value of Sn expressed under an expression (1) concerning inclination of an accumulated pore capacity distribution curve of the porous bulkhead 2 (curve expressed with a graph with a lateral axis as the pore diameter and a vertical axis as accumulated pore capacity) namely Sn=-(Vn-Vn-1)/(log(Dn)-log(Dn-1)) (1), (where, Dn is a pore diameter (μm) at a No.(n) measuring point, Dn-1 is a pore diameter (μm) at a No.(n-1) measuring point, Vn is accumulated pore capacity (cm3/g) at the number (n) measuring point, Vn-1 is accumulated pore capacity (cm3/g) at the No.(n-1) measuring point and Sn is inclination of the accumulated pore capacity distribution curve against the pore diameter at the No.(n) measuring point).



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Ｂ０１Ｄ　39/20		Ｂ０１Ｄ　39/20	Ｄ　４Ｄ０１９
Ｃ０４Ｂ　38/00	３０３	Ｃ０４Ｂ　38/00	３０３Ｚ　４Ｄ０５８
// Ｂ０１Ｄ　46/00	３０２	Ｂ０１Ｄ　46/00	３０２　４Ｇ０１９

審査請求　有　請求項の数６　ＯＬ　（全 11 頁）

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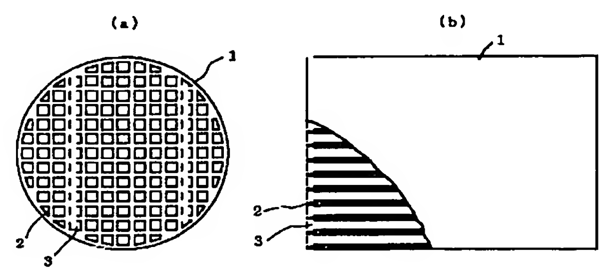
最終頁に続く

(54)【発明の名称】　セラミックハニカムフィルタ

(57)【要約】　（修正有）

【課題】　低圧力損失、高捕集効率、高耐久性のディーゼル機関の排気微粒子捕集用セラミックハニカムフィルタの提供

【解決手段】　セラミックハニカム構造体１の多孔質隔壁は６０％以上の気孔率、１５μm以上の平均細孔径を有し、前記多孔質隔壁２の累積細孔容積分布曲線（横軸を細孔径とし、縦軸を累積細孔容積とするグラフで表される曲線）の傾きに関する下記式（１）　$S_n = -(V_n - V_{n-1}) / (\log(D_n) - \log(D_{n-1}))$　（１）、（但し、D_nは（ｎ）番目の測定点における細孔径（μm）であり、D_{n-1}は（ｎ－１）番目の測定点における細孔径（μm）であり、V_nは（ｎ）番目の測定点における累積細孔容積（cm^3/g）であり、V_{n-1}は（ｎ－１）番目の測定点における累積細孔容積（cm^3/g）であり、S_nはｎ番目の測定点における細孔径に対する累積細孔容積分布曲線の傾きである。）により表されるS_nの最大値が０．７以上であること特徴とする。



【特許請求の範囲】

【請求項1】　セラミックハニカム構造体の所定の流路端部を目封止し、該流路を区画する多孔質の隔壁に排気ガスを通過せしめることにより、排気ガス中に含まれる微粒子を除去するセラミックハニカムフィルタにおいて、前記多孔質隔壁は水銀圧入法により測定した場合に６０％以上の気孔率、１５μm以上の平均細孔径を有し、n番目の測定点における細孔径に対する前記隔壁の累積細孔容積分布曲線の傾きS_nの最大値は０．７以上であり、前記累積細孔容積分布曲線の傾きS_nは下記式（１）

$$S_n = -(V_n - V_{n-1}) / (\log(D_n) - \log(D_{n-1})) \quad (1)、$$

（但し、D_nは（ｎ）番目の測定点における細孔径（μm）であり、D_{n-1}は（ｎ－１）番目の測定点における細孔径（μm）であり、V_nは(n)番目の測定点における累積細孔容積（cm^3/g）であり、V_{n-1}は(n－1)番目の測定点における累積細孔容積（cm^3/g）である。）により表されることを特徴とするセラミックハニカムフィルタ。

【請求項2】　前記多孔質隔壁の累積細孔分布容積曲線における傾きS_nの最大値が０．９以上であることを特徴とする請求項１項記載のセラミックハニカムフィルタ。

【請求項3】　前記多孔質隔壁の気孔率が６０～８０％であることを特徴とする請求項１乃至２記載のセラミックハニカムフィルタ。

【請求項4】　前記多孔質隔壁の平均細孔径が１５～４０μmであることを特徴とする請求項１乃至３記載のセラミックハニカムフィルタ。

【請求項5】　前記多孔質隔壁を構成する多孔質セラミックスの主成分の化学組成がSiO_2：４２～５６質量%、Al_2O_3：３０～４５質量%、MgO：１２～１６質量%で、結晶相の主成分がコージェライトであることを特徴とする請求項１乃至４記載のセラミックハニカムフィルタ。

【請求項6】　セラミックハニカム構造体の所定の流路端部を目封止し、該流路を区画する多孔質の隔壁に排気ガスを通過せしめることにより、排気ガス中に含まれる微粒子を除去するセラミックハニカムフィルタであって、前記多孔質隔壁表面及び多孔質隔壁内部に触媒が担持されているセラミックハニカムフィルタにおいて、前記多孔質隔壁は水銀圧入法により測定した場合に６０％以上の気孔率、１５μm以上の平均細孔径を有し、n番目の測定点における細孔径に対する前記隔壁の累積細孔容積分布曲線の傾きS_nの最大値は０．７以上であり、前記累積細孔容積分布曲線の傾きS_nは下記式（１）

$$S_n = -(V_n - V_{n-1}) / (\log(D_n) - \log(D_{n-1})) \quad (1)、$$

（但し、D_nは（ｎ）番目の測定点における細孔径（μm）であり、D_{n-1}は（ｎ－１）番目の測定点における細孔径（μm）であり、V_nは(n)番目の測定点における累積細孔容積（cm^3/g）であり、V_{n-1}は(n－1)番目の測定点における累積細孔容積（cm^3/g）である。）により表されることを特徴とするセラミックハニカムフィルタ。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、ディーゼル機関の排出ガス中に含まれる微粒子を除去するためのセラミックハニカムフィルタに関するものである。

【０００２】

【従来の技術】ディーゼル機関から排出される微粒子を除去するため、セラミックハニカム構造体の隔壁を多孔質構造とし、その隔壁に微粒子を含んだ排気ガスを通過せしめる構造の微粒子捕集用フィルタ（ディーゼルパティキュレートフィルタ）を採用する検討が進められている。このフィルタの特性に関しては、微粒子の捕集効率、圧力損失（圧損）、微粒子の捕集時間（捕集開始から一定圧損に達するまでの時間）の３つが重要とされている。中でも、捕集効率と圧損は相反する関係にあり、捕集効率を高くしようとすると、圧損が増大し、捕集時間が短くなり、また圧損を低くすると、捕集時間は長くできるが、捕集効率が悪くなる。これらの相反するフィルタの特性を満足するように、セラミックハニカム構造体に対しては、下記のように、気孔率、平均細孔径、隔壁表面に存在する細孔の大きさを制御する技術が従来から検討されてきた。

【０００３】特公平３－１０３６５号公報では、フィルタ隔壁表面に存在する細孔を、孔径５～４０μmの小孔と、孔径４０～１００μmの大孔とから構成し、該小孔の数が該大孔の数の５～４０倍となるように構成することにより、捕集効率を初期から高い値に維持できると共に、圧力損失の低い排ガス浄化用フィルタの得られることが開示されている。一方、隔壁内部に存在する内部細孔の平均孔径は１５μmより大きく、かつ累積細孔容積は０．３～０．７cm^3/gが好ましい範囲となっている。ここで、隔壁の気孔率P(体積%)の記載はないが、実施例に記載されているコージェライト材料の真比重ρを２．５g/cm^3とすると、累積細孔容積V（cm^3/g）から以下の計算式で算出することができる。$P = 100 \times V \times \rho / (1 + V \times \rho)$。従って、隔壁内部に存在する内部細孔の累積細孔容積の好ましい範囲０．３～０．７cm^3/gは、気孔率に換算すると４２．８～６３．６体積%となる。（特許文献１参照。）

また、特公昭６１－５４７５０号公報には、オープンポロシティ（気孔率）と平均細孔径を制御することによって、高捕集率タイプから低捕集率タイプまでのフィルタを設計しうることが開示されている。本公報での好適な

具体例として、第２０頁の図８の点１－５－６－４を結ぶ境界内に限定される帯域内のオープンポロシティ（気孔率）及び平均気孔径(平均細孔径)が記載されている。ここで点１はオープンポロシティ５８．５容量％、平均気孔直径１μｍ、点５はオープンポロシティ３９．５容量％、平均気孔直径１５μｍ、点６は、オープンポロシティ６２．０容量％、平均気孔直径１５μｍ、点４はオープンポロシティ９０．０容量％、平均気孔直径１μｍである。（特許文献２参照。）
そして、特開平９－７７５７３号公報には、気孔率５５～８０％、平均細孔径が２５～４０μmであり、かつ隔壁表面の細孔は５～４０μmの小孔と４０～１００μmの大孔とよりなり、該小孔の数を該大孔の数の５～４０倍とすることにより、高捕集率、低圧損、かつ低熱膨張率の特性を合わせもつハニカム構造体の得られることが開示されている。（特許文献３参照。）

【０００４】

【特許文献１】特公平３－１０３６５号公報
【特許文献２】特公昭６１－５４７５０号公報（図８）
【特許文献３】特開平９－７７５７３号公報

【０００５】

【発明が解決しようとする課題】しかしながら、上記従来の技術に示す如く気孔率、平均細孔径、隔壁表面の孔の大きさの最適化により、気孔率と捕集効率のバランスはある程度達成できるものの、隔壁自体が多孔質体であり、多孔質体の強度はその気孔率、平均細孔径と相反する関係にあることから、セラミックハニカム構造体の強度は、必然的に低下することになる。即ち、気孔率や細孔の大きさが大きくなると、セラミックハニカム構造体の強度は低下するのである。特に低圧力損失のフィルタを得るために、気孔率を６０％以上、或いは平均細孔径を１５μｍ以上にした場合は、強度低下が顕著になる。このため、低圧力損失と高捕集効率を両立させ、しかもディーゼル機関の微粒子捕集用フィルタとして使用した場合に発生する熱応力や熱衝撃応力、組立時の機械的締め付け力や振動による応力等により破損することなく、長期にわたり耐久性のあるセラミックハニカムフィルタが得られないという問題があり、ディーゼルパティキュレートフィルタの実用化の障害になっていた。

【０００６】本発明は、上記問題を解決するため、低圧力損失のフィルタが得られるように、隔壁の気孔率を６０％以上、平均細孔径１５μｍ以上としても、ディーゼル機関の微粒子捕集用フィルタとして使用した場合に発生する熱応力や熱衝撃応力、組立時の機械的締め付け力や振動による応力等により破損することなく、長期にわたり耐久性を有するセラミックハニカムフィルタを提供することを目的とする。

【０００７】

【課題を解決するための手段】上記課題を解決するため、本発明者は鋭意検討を行った結果、ハニカム構造体の隔壁に形成される細孔の分布をある一定範囲内とすることにより、低圧力損失、高捕集効率、さらには高強度の３つの特性を満足させたセラミックハニカムフィルタが得られることを見出し、本発明に想到した。すなわち、本発明のセラミックハニカムフィルタは、セラミックハニカム構造体の所定の流路端部を目封止し、該流路を区画する多孔質の隔壁に排気ガスを通過せしめることにより、排気ガス中に含まれる微粒子を除去するセラミックハニカムフィルタにおいて、前記多孔質隔壁は水銀圧入法により測定した場合に６０％以上の気孔率、１５μｍ以上の平均細孔径を有し、前記多孔質隔壁の累積細孔容積分布曲線の傾きに関する下記式（１）

$$S_n = -(V_n - V_{n-1}) / (\log(D_n) - \log(D_{n-1})) \quad (1),$$

（但し、D_nは（ｎ）番目の測定点における細孔径（μｍ）であり、D_{n-1}は（ｎ－１）番目の測定点における細孔径（μｍ）であり、V_nは(n)番目の測定点における累積細孔容積（ｃｍ³／ｇ）であり、V_{n-1}は(n－1)番目の測定点における累積細孔容積（ｃｍ³／ｇ）であり、S_nはn番目の測定点における細孔径に対する累積細孔容積分布曲線の傾きである。）により表されるS_nの最大値が０．７以上であることを特徴とする。この時、S_nの最大値は０．９以上であることが好ましく、気孔率は６０～８０％、平均細孔径は１５～４０μｍであることが好適である。さらに、隔壁を構成する多孔質セラミックスの主成分の化学組成がSiO_2：４２～５６質量％、Al_2O_3：３０～４５質量％、MgO：１２～１６質量％で、結晶相の主成分がコージェライトであることが好適である。また、本発明のセラミックハニカムフィルタは、セラミックハニカム構造体の所定の流路端部を目封止し、該流路を区画する多孔質の隔壁に排気ガスを通過せしめることにより、排気ガス中に含まれる微粒子を除去するセラミックハニカムフィルタであって、前記多孔質隔壁表面及び多孔質隔壁内部に触媒が担持されているセラミックハニカムフィルタにおいて、前記多孔質隔壁は水銀圧入法により測定した場合に６０％以上の気孔率、１５μｍ以上の平均細孔径を有し、前記多孔質隔壁の累積細孔容積分布曲線の傾きに関する下記式（１）

$$S_n = -(V_n - V_{n-1}) / (\log(D_n) - \log(D_{n-1})) \quad (1),$$

（但し、D_nは（ｎ）番目の測定点における細孔径（μｍ）であり、D_{n-1}は（ｎ－１）番目の測定点における細孔径（μｍ）であり、V_nは(n)番目の測定点における累積細孔容積（ｃｍ³／ｇ）であり、V_{n-1}は(n－1)番目の測定点における累積細孔容積（ｃｍ³／ｇ）であり、S_nはn番目の測定点における細孔径に対する累積細孔容積分布曲線の傾きである。）により表されるS_nの最大値が０．７以上であることを特徴とする。

【0008】

【作用】次に、本発明における作用効果につき説明する。本発明のセラミックハニカムフィルタでは、セラミックハニカム構造体の多孔質隔壁は水銀圧入法により測定した場合に60%以上の気孔率、15μm以上の平均細孔径を有し、前記多孔質隔壁の累積細孔容積分布曲線（横軸を細孔径とし、縦軸を累積細孔容積とするグラフで表される曲線）の傾きに関する下記式（1）

$$S_n = -(V_n - V_{n-1}) / (\log(D_n) - \log(D_{n-1})) \quad (1)、$$

（但し、D_nは（n）番目の測定点における細孔径（μm）であり、D_{n-1}は（n−1）番目の測定点における細孔径（μm）であり、V_nは(n)番目の測定点における累積細孔容積（cm^3/g）であり、V_{n-1}は(n−1)番目の測定点における累積細孔容積（cm^3/g）であり、S_nはn番目の測定点における細孔径に対する累積細孔容積分布曲線の傾きである。）により表されるS_nの最大値が0.7以上であることから、高気孔率で細孔分布がシャープとなり、平均細孔径を中心とした細孔の占める割合が多くなるため、圧力損失が低く抑えられると共に、強度を高く維持することが可能となるのである。ここで、累積細孔容積分布曲線の傾きS_nを限定した理由について詳細に説明する。セラミックハニカム構造体の強度は、気孔率や平均細孔径の影響を受けるのは勿論であるが、細孔径分布に依存することが大きく、特に細孔径分布をシャープに、言い換えれば細孔寸法の均一性を向上させることにより、気孔率が60%以上、平均細孔径15μm以上であっても高強度の得られることを見出したことによる。ここで気孔率、平均細孔径、累積細孔容積分布曲線の傾きS_nは、Micromeritics社製のオートポアIII9410を使用し、水銀圧入法で測定した。この水銀圧入法の測定においては、測定用の試料を測定セル内に収納し、セル内を減圧した後、水銀を導入して、加圧し、このときの圧力と試料内に存在する細孔中に押し込まれた水銀の体積との関係から、細孔径と累積細孔容積の関係を求める。即ち、加圧力が大きいと、より微細な細孔にまで水銀が浸入し、加圧力に相当する微細な細孔の容積が測定される。このため、測定は、細孔径の大きいものから小さいものへと順次行われる。このとき、測定開始から、（n−1）番目の測定点における細孔径D_{n-1}、及び累積細孔容積V_{n-1}と、（n）番目の測定点における細孔径D_nと累積細孔容積V_nから、上記式（1）により求めたものが、（n）番目の測定点における傾きS_nとなる。S_nの測定結果の一例を図3に示す。図3において点aは1番目と2番目の測定点における細孔径D_1、D_2及び累積細孔容積V_1、V_2から求めた傾きS_1 [$(V_1 - V_2) / (\log D_1 - \log D_2)$] であり、点bは2番目と3番目の測定点における細孔径D_2、D_3及び累積細孔容積V_2、V_3から求めた傾きS_2 [$(V_2 - V_3) / (\log D_2 - \log D_3)$] である。ここで、図3に示す細孔径と累積細孔容積分布曲線の傾きS_nの分布から、S_nの最大値が0.7未満であると細孔径分布はブロードであり、S_nの最大値が0.7以上であればと細孔径分布は非常にシャープであることが分かる。細孔径分布がブロードであると、強度低下の原因である粗大細孔や、微粒子が目詰まりして圧損増大の原因となる微細細孔の割合が低下し、低圧損と高強度の両立が困難なるが、S_nの最大値が0.7以上になると、細孔径分布がシャープになるので、粗大細孔や微細細孔の割合が低下し、低圧損と高強度の両立が達成できる。これは、累積細孔容積分布曲線の傾きS_nの最大値とA軸圧縮強度比の関係を示す図4からも明らかである。、ここで、A軸圧縮強度比とは従来品レベルを1.0として求めたA軸圧縮強度の相対値である。S_nの最大値が0.7以上になると、A軸圧縮強度は従来品レベル（例えばS_nの最大値が0.6以下の領域）の1.5以上となることが判る。すなわち、S_nの最大値が0.7以上になると、セラミックハニカム構造体の機械的強度は著しく向上することが分かる。低圧力損失と高強度を両立させるためにはS_nの最大値は0.9以上がより好ましい。ここで、セラミックハニカム構造体の気孔率を60%以上に限定するのは、気孔率が60%未満ではフィルタの圧力損失が高くなるからである。また、気孔率が80%を越えると、フィルタの強度が低下すると共に、微粒子の捕集効率も悪くなるから気孔率60〜80%が好ましい範囲である。さらには、気孔率65%以上で、圧力損失を低減する効果が更に大きくなり、気孔率75%以下で、強度や捕集効率の低下をより小さくできることから気孔率65〜75%がより好ましい範囲である。また、セラミックハニカム構造体中に存在する細孔の平均細孔径を15μm以上に限定するのは、平均細孔径が15μm未満ではフィルタの圧力損失が大きくなってしまうからである。また、平均細孔径が40μmを超える場合、フィルタの強度が低下すると共に、小さな微粒子が捕捉されずにフィルタを通過してしまい捕集効率が悪くなるから平均細孔径15〜40μmが好ましい範囲である。さらに、平均細孔径25μm以下で、強度や捕集効率の低下をより小さくできることから、平均細孔径15〜25μmが低圧力損失と高強度の相反する特性の両立が達成できるより好ましい範囲である。

【0009】そして、本発明のセラミックハニカムフィルタにおいて、ハニカム構造体の隔壁を構成する多孔質セラミックスの主成分の化学組成がSiO_2：42〜56質量%、Al_2O_3：30〜45質量%、MgO：12〜16質量%で、結晶相の主成分がコージェライトであることが好適としたのは、元来コージェライトが有する低熱膨張性を利用し、熱衝撃が加わってもクラックの発生しにくいセラミックハニカムフィルタが得られるからであるが、本発明はこれに限定されるものではなく、

その他の耐熱性セラミックス、例えば、ムライト、アルミナ、窒化珪素、炭化珪素、窒化アルミ、リチウムアルミニウムシリケート、チタン酸アルミニウム、ジルコニア、等の材料を使用することができる。

【0010】また、多孔質隔壁表面及び多孔質隔壁内部に触媒が担持されているセラミックハニカムフィルタにおいて、セラミックハニカム構造体の多孔質隔壁は水銀圧入法により測定した場合に60%以上の気孔率、15μm以上の平均細孔径を有し、前記多孔質隔壁の累積細孔容積分布曲線（横軸を細孔径とし、縦軸を累積細孔容積とするグラフで表される曲線）の傾きに関する下記式（1）

$$S_n = -(V_n - V_{n-1}) / (\log(D_n) - \log(D_{n-1})) \quad (1)、$$

（但し、D_nは（n）番目の測定点における細孔径（μm）であり、D_{n-1}は（n－1）番目の測定点における細孔径（μm）であり、V_nは(n)番目の測定点における累積細孔容積（cm^3/g）であり、V_{n-1}は(n－1)番目の測定点における累積細孔容積（cm^3/g）であり、S_nはn番目の測定点における細孔径に対する累積細孔容積分布曲線の傾きである。）により表されるS_nの最大値が0．7以上であることから、前述したような低圧力損失、高捕集効率、高強度を両立させる効果が、隔壁表面及び隔壁内部に触媒が担持されているセラミックハニカムフィルタにおいて顕著であるからである。

【0011】本発明のセラミックハニカム構造体は、以下のようにして製造することが出来る。まずセラミックス原料粉末に、平均粒径20μm以上、特に粒径20～100μmが50%以上を占める造孔材を焼成後の気孔率が60～80%得られる範囲で添加する。この混合物に対して必要に応じてバインダー、潤滑剤等の成形助剤を加え、混合した後、水を添加して可塑化可能なバッチを作製する。このバッチを公知の押出成形法によりハニカム構造の成形体を押出し成形した後、乾燥、造孔材の燃焼除去、焼成を行うことにより、隔壁中にセラミックス固有の微細孔及び造孔材燃焼除去後の痕跡により形成された細孔を有するハニカム構造体を得る。このように、セラミックスが元来保有する微細孔と粒径が揃った造孔材（平均粒径20μm以上で、粒径20～100μmが50%以上を占める）により形成された細孔との組合せにより、隔壁の平均細孔径を15～25μmの範囲に収めることが出来るのと共に、細孔分布のシャープさを示すSnの最大値を0．7以上とすることができる。特に、コージェライト質セラミックスは、元来1～20μm程度の細孔径の細孔を有すので、平均粒径20μm以上で、粒径20～100μmが50%以上を占める造孔材との組合せが有効である。なお造孔材は、公知のグラファイト、小麦粉、樹脂粉末等であり、平均粒径20μm以上、粒径20～100μmが50%以上を占める粒度分布となるように分級するのが好ましい。また樹脂粉末を使用する場合、その製造条件を調整して、平均粒径20μm以上、粒径20～100μmが50%以上を占める粒度分布としても良い。また、造孔材は略球状であると、隔壁中に形成される細孔も略球状となることから、細孔への応力集中を低減することができ、優れた機械的強度を有するセラミックハニカム構造体が得られることから好ましい。更には造孔材が中空であると、造孔材を燃焼除去する際に、容易に隔壁中から除去することが可能となり、燃焼除去の際に隔壁に亀裂が入るといった問題が起こり難く、製造歩留まりが向上することから好ましい。

【0012】

【発明の実施の形態】以下、本発明の実際の実施例を説明するが、本発明はそれらに限定されるものではない。

（実施例1）SiO_2が42～56質量%、Al_2O_3が30～45質量%、MgOが12～16質量%となるようにカオリン、仮焼カオリン、アルミナ、水酸化アルミニウム、シリカ、タルク等のコージェライト化セラミック原料粉末にバインダー、潤滑剤、及び造孔材としてNo．1～3の3種類の球状樹脂粉末をそれぞれ所定量混合した。この時、造孔材として使用した球状樹脂粉末の粒度分布を図5に、また平均粒径及び20～100μmの粒径の割合を表1に示す。次に、この混合物に水を添加して可塑化可能なバッチを作製し、このバッチを公知の押出成形法により、円筒形ハニカム構造体を成形した。次いでこの成形体を乾燥した上で1380～1420℃の温度域で焼成して、第1図(a)、(b)の正面図及び側面図に示すように、多孔質セラミック隔壁3と貫通孔2からなり、造孔材No．1～3に対応した試験No．1～3の3種類のコージェライト質セラミックハニカム構造体1を得た。得られたハニカム構造体の直径は143mm、長さ152mmで、隔壁の壁厚が0．3mm、1cm^2当たりの流路の数が46個であった。

【0013】得られた試験No．1～3の3種類のコージェライト質セラミックハニカム構造体の気孔率、平均細孔径、累積細孔容積分布曲線の傾きS_nをMicromeritics社製のオートポアIII9410を使用し、水銀圧入法で測定した。測定で得られた数値は、試料に加えた水銀の圧力と試料中に圧入された水銀の体積であるが、（n）番目の測定点の細孔径D_nは（2）式より、（n）番目の測定点の累積細孔容積V_nは（3）式より計算した。

$$(n)番目の測定点の細孔径 D_n = -4\alpha\cos\theta / Pn \quad (2)$$

ここで、αは、水銀の表面張力（4．935×10－4 kg／cm）

θは、水銀と固体の接触角（130°）

Pnは、（n）番目の測定点の水銀の圧力である。

（ｎ）番目の測定点の累積細孔容積$V_n = v_n / w$　　　（３）

ここで、v_nは、（ｎ）番目の測定点の試料中に圧入された試料の体積ｗは、試料の重量である。得られた細孔径と累積細孔容積との関係（累積細孔容積分布曲線）を図６に示す。図６から明らかなように、約１０μｍ～約１００μｍの間で、試験Ｎｏ．１のハニカム構造体の累積細孔容積分布曲線の傾きは非常に急峻であり、試験Ｎｏ．２のハニカム構造体の累積細孔容積分布曲線の傾きも急峻であるが、試験Ｎｏ．３のハニカム構造体の累積細孔容積分布曲線の傾きは比較的緩やかであった。上記と図６に示す累積細孔容積分布曲線から、試験Ｎｏ．１～３のハニカム構造体の累積細孔容積分布曲線の傾きS_nを求めた。累積細孔容積分布曲線の傾きS_nは、測定データのプロットから滑らかな近似曲線を求め、その曲線上で細孔径の微小間隔における微分値として求めるべきところであるが、図６から明らかなように、累積細孔分布曲線は十分に滑らかであり、且つ測定点は細孔径の対数（$\log D_n$）に関して実質的に等間隔であるので、（ｎ）番目の測定点と（ｎ－１）番目の測定点における細孔径、および累積細孔容積の測定値から、傾きS_nを求めても、誤差は殆どない。このようにして得られた各ハニカム構造体の細孔径と累積細孔容積分布曲線の傾きＳｎの関係を図７に示す。図６の累積細孔容積分布曲線で傾きが最も急峻であった試験Ｎｏ．１のハニカム構造体のＳｎが最も高く、次に急峻であった試験Ｎｏ．２のハニカム構造体のS_nが次に高く、傾きが比較的緩やかであった試験Ｎｏ．３のハニカム構造体のS_nは最も小さかった。このようにして求めたＳｎの最大値、及び気孔率、平均細孔径の測定結果を表２に記載した。

【００１４】

【表１】

造孔材	平均粒径（μｍ）	20-100μｍの粒径の割合（質量%）
No.1	64	75
No.2	62	62
No.3	52	48

【００１５】上記のように作製したセラミックハニカム構造体の端面を、第２図（ａ）、（ｂ）にその正面図及び側面図を示すように封じ材５により目封じし、多孔質セラミックハニカムフィルタを得た。この得られた多孔質セラミックハニカムフィルターのフィルター特性を、圧損、耐破損性について評価を行った その結果を合せて表２に示す

ここで、圧損は、圧力損失テストスタンドにて所定流量の空気を流した時のハニカムフィルター流入前と流出後の圧力損失で評価を行ない、実用的に許容される値以下の圧力損失であれば合格とし（○）で、実用的に許容される圧力損失を超える圧力損失であれば不合格とし（×）で示した。耐破損性は、Ａ軸圧縮強度比の値で評価し、これが従来品レベルを１．０として、１．５以上の場合は合格とし（○）で、更に２．０以上の好ましい場合は(◎)で、１．５未満の場合には不合格とし（×）で示した。 また、Ａ軸圧縮強度の測定は、社団法人自動車技術会が定める規格Ｍ５０５－８７「自動車排気ガス浄化触媒用セラミックモノリス担体の試験方法」に従って行った。そして、総合判定として、圧損、耐破損性のいずれも合格であるものを（○）、そのうち（◎）判定があった場合は（◎）、いずれか１つでも不合格であるものを（×）で評価した。

【００１６】

【表２】

試験No		隔壁の材料特性			フィルター特性		総合判定
		気孔率(%)	平均細孔径(μｍ)	累積細孔容積分布曲線の傾きSnの最大値	圧力損失	耐破損性	
試験No.1	本発明例	65.0	20.8	1.12	○	◎	◎
試験No.2		66.4	22.0	0.85	○	○	○
試験No.3	比較例	67.3	19.5	0.66	○	×	×

【００１７】表２に示す結果のうち、本発明例である試験Ｎｏ．１～２に示すセラミックハニカムフィルタでは、累積細孔容積分布曲線における傾きS_nの最大値が０．７以上であることから、気孔率が６０％以上、平均細孔径が１５μｍ以上という多孔質材料であっても、圧力損失が低く、耐破損性についても合格し、総合判定は（○）及び（◎）であった。一方、表２に示す結果のうち、比較例の試験Ｎｏ.３に示すセラミックハニカムフィルタは、累積細孔容積分布曲線における傾きS_nの最大値が０．７を下まわったことから、圧力損失は合格し

たが、耐破損性は不合格（×）となり、総合判定は（×）であった。以上、表２の結果から明らかなように、微粒子捕集用フィルターとして重要な特性である圧力損失、耐破損性の結果から総合判定すると、本発明の実施例である試験Ｎｏ．１～２のセラミックハニカムフィルタはいずれも圧損特性、耐破損性を満足するフィルタであった。

【００１８】（実施例２）実施例１の試験Ｎｏ．１と同様の可塑化可能なバッチを作製し、このバッチを公知の押出成形法により、円筒形ハニカム構造体を成形した。この際各種の隔壁厚さ、１ｃｍ² 当たりの流路の数が得られるよう公知の金型の寸法を調整した。次いでこの成形体を乾燥した上で１３８０～１４２０℃の温度域で焼成して、多孔質セラミック隔壁３と貫通孔２からなる各種コージェライト質セラミックハニカム構造体１を得た。得られたハニカム構造体の直径は１４３ｍｍ、長さ１５２ｍｍで、試験Ｎｏ．４～８に示すように隔壁の壁厚が０．１５ｍｍ～０．３３ｍｍ、１ｃｍ² 当たりの流路の数が３９～６２個での５種類であった。以下、実施例１と同様の方法により、端面の目封じを行った上で、フィルター特性である圧損と耐破損性についての測定を行った。その結果を表３に示す。なお、試験Ｎｏ．４～８のいずれも、気孔率は６５％、平均細孔径は２０．８％、累積細孔容積分布曲線における傾きS_nの最大値は１．１２であった。

【００１９】

【表３】

試験 No		隔壁構造		フィルター特性		総合判定
		壁厚 (mm)	流路の数 (個/cm²)	圧力損失	耐破損性	
試験 No.4	本発明例	0.15	46	○	○	○
試験 No.5		0.2	46	○	○	○
試験 No.6		0.33	46	○	◎	◎
試験 No.7		0.3	62	○	◎	◎
試験 No.8		0.3	39	○	○	○

【００２０】表３に示すように、本発明例である試験Ｎｏ．４～８に示すセラミックハニカムフィルタは、いずれの隔壁構造であっても、フィルター特性の総合判定は（○）、または（◎）であった。

【００２１】（実施例３）実施例１で使用した、試験Ｎｏ．１～３のセラミックハニカムフィルタに対して以下のように隔壁表面及び内部に触媒を担持した。

【００２２】高比表面積材料として、中心粒径５μｍの活性アルミナとアルミナゾルを水と共に混合し、撹拌した活性アルミナスラリーに得られたフィルタをウオッシュコートした。その後、余分に付着したスラリーを取り除き、コーティングを繰り返して、コート量６０ｇ／Ｌのフィルタを作製した。さらにその後、１２０℃で乾燥させた後、８００℃で焼成後、塩化白金酸水溶液中に浸積し、１２０℃で乾燥させた後、８００℃で焼成して、白金を担持させたセラミックハニカムフィルタを得た。このときの白金の担持量は約２ｇ／Ｌであった。

【００２３】この触媒担持後のセラミックハニカムフィルタのフィルタに対して、実施例１と同様の方法により圧力損失を測定した。さらに、圧力損失テストスタンドにて所定流量に、所定量のカーボンを投入し、ハニカムフィルターにカーボンを捕捉させた際の、カーボン捕捉前後の圧力損失差ΔＰ（カーボン捕捉後の圧力損失―カーボン捕捉前の圧力損失）の測定を行い、圧力損失差ΔＰが実用的に許容される値以下であれば合格とし（○）で、実用的に許容される値を超える圧力損失であれば不合格とし（×）で示した。結果を合せて表４に示す。

【００２４】

【表４】

試験 No		触媒担持後の圧力損失	触媒担持後 カーボン捕捉試験前後の圧力損失差ΔP
試験 No.1	本発明例	○	○
試験 No.2		○	○
試験 No.3	比較例	×	×

【００２５】表４に示す結果のうち、本発明例である試験Ｎｏ．１～２に示すセラミックハニカムフィルタは、触媒担持による圧力損失の上昇は殆ど認められず、圧力損失の結果はすべて合格（○）となった。一方、比較例である試験Ｎｏ．３に示すセラミックハニカムフィルタは、触媒担持により圧力損失の上昇が認められ圧力損失の結果は不合格（×）となった。また、本発明例である試験Ｎｏ．１～２に示すセラミックハニカムフィルタ

は、カーボン捕捉前後の圧力損失差ΔＰが実用的に許容される値未満で合格（○）となっが、比較例である試験Ｎｏ．３に示すハニカムフィルタはΔＰが実用的に許容される値を越えて不合格（×）となった。以上の様に、累積細孔容積分布曲線における傾きS_nの最大値が０．７以上であるセラミックハニカムフィルタは、触媒担持後においても、圧力損失の上昇や、カーボン捕捉による圧力損失上昇が小さく優れたフィルタ性能を示すことは明白である。

【００２６】

【発明の効果】本発明によれば、セラミックハニカムフィルタを構成するセラミックハニカム構造体の隔壁中の細孔の累積細孔容積分布曲線における傾きS_nの最大値を０．７以上とすることにより、気孔率が６０％以上、平均細孔径が１５μｍ以上の高い値であっても、ディーゼルパティキュレートフィルタとして使用した際に、相反する性質である、低圧力損失と高捕集効率の両特性を両立させることが可能である。しかも使用時の熱応力や熱衝撃応力、組立持の機械的締め付け力や振動による応力に対しても破損しない、耐久性に優れたセラミックハニカムフィルタが得られる。

【図面の簡単な説明】

【図１】（ａ）及び（ｂ）はそれぞれハニカム構造体の一例を示す正面図及び側面図である。

【図２】（ａ）及び（ｂ）はそれぞれハニカム構造体を使用したフィルターの一例を示す正面図及び側面図である。

【図３】　水銀圧入法により求めた細孔径と累積細孔容積分布曲線の傾きS_nとの関係を示す一例のグラフである。

【図４】　累積細孔容積分布曲線の傾きS_nの最大値とＡ軸圧縮強度比との関係を示す一例のグラフである。

【図５】　実施例１で使用した造孔材の粒度分布を示すグラフである。

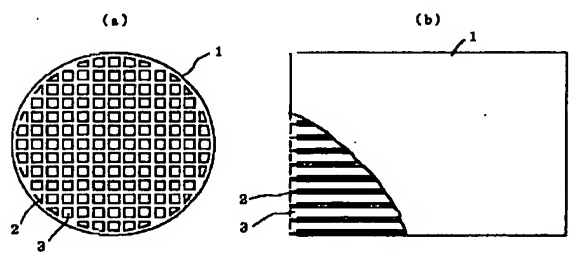
【図６】　実施例１における試験Ｎｏ．１～３の試験片の細孔径と累積細孔容積との関係を示すグラフである。

【図７】　実施例１における試験Ｎｏ．１～３の試験片の細孔径と累積細孔容積分布曲線の傾きS_nとの関係を示すグラフである。

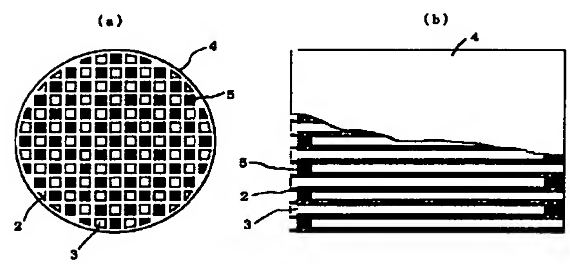
【符号の説明】

１：セラミックハニカム構造体、　２：隔壁、　３：貫通孔、４：セラミックハニカムフィルタ、５：封じ材、ａ：累積細孔容積分布曲線における１番目と２番目の測定結果から求めた傾きS_1、ｂ：累積細孔容積分布曲線における２番目と３番目の測定結果から求めた傾きS_2、

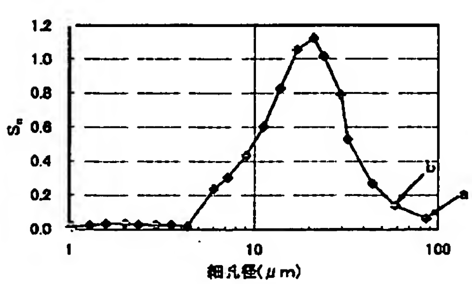
【図１】



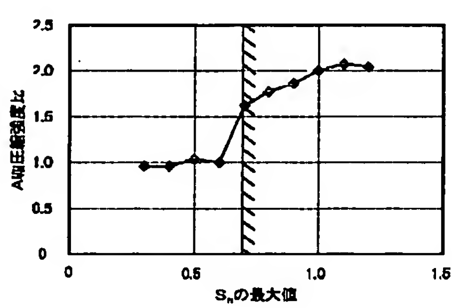
【図２】



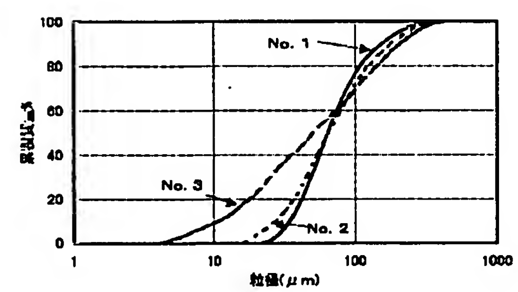
【図３】



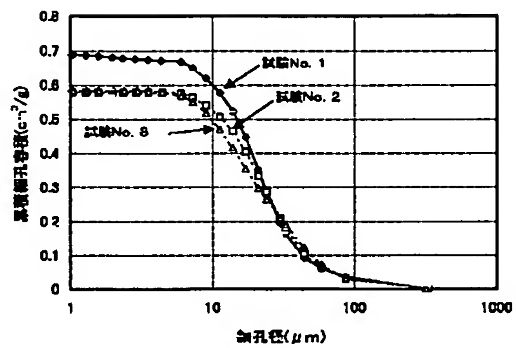
【図４】



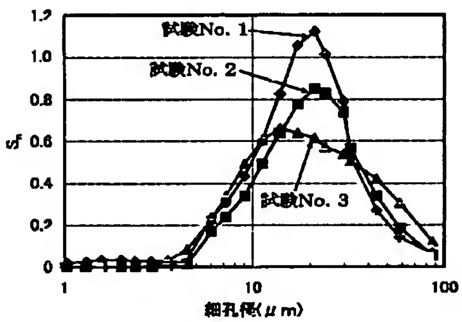
【図5】



【図6】



【図7】



【手続補正書】
【提出日】平成15年4月15日（2003．4．15）
【手続補正1】
【補正対象書類名】明細書
【補正対象項目名】特許請求の範囲
【補正方法】変更
【補正内容】
【特許請求の範囲】
【請求項１】　セラミック原料粉末に、平均粒径２０μm以上、粒径２０～１００μmが５０％以上の粒度分布を有する造孔材を少なくとも添加した後、水等を添加混合したバッチを、押出成形後、乾燥、焼成して得られるセラミックハニカム構造体の所定の流路端部を目封止し、該流路を区画する多孔質の隔壁に排気ガスを通過せしめることにより、排気ガス中に含まれる微粒子を除去するセラミックハニカムフィルタにおいて、前記多孔質隔壁は水銀圧入法により測定した場合に６０％以上の気孔率、１５μm以上の平均細孔径を有し、n番目の測定点における細孔径に対する前記隔壁の累積細孔容積分布曲線の傾きS_nの最大値は０．７以上であり、前記累積細孔容積分布曲線の傾きS_nは下記式（１）

$$S_n = -(V_n - V_{n-1}) / (\log(D_n) - \log(D_{n-1})) \quad (1)、$$

（但し、D_nは（n）番目の測定点における細孔径（μm）であり、D_{n-1}は（n−１）番目の測定点における細孔径（μm）であり、V_nは(n)番目の測定点における累積細孔容積（cm^3／g）であり、V_{n-1}は(n−1)番目の測定点における累積細孔容積（cm^3／g）である。）により表されることを特徴とするセラミックハニカムフィルタ。
【請求項２】　前記多孔質隔壁の累積細孔分布容積曲線における傾きS_nの最大値が０．９以上であることを特徴とする請求項１項記載のセラミックハニカムフィルタ。
【請求項３】　前記多孔質隔壁の気孔率が６０～８０％であることを特徴とする請求項１乃至２記載のセラミックハニカムフィルタ。
【請求項４】　前記多孔質隔壁の平均細孔径が１５～４０μmであることを特徴とする請求項１乃至３記載のセラミックハニカムフィルタ。
【請求項５】　前記多孔質隔壁を構成する多孔質セラミックスの主成分の化学組成がSiO_2：４２～５６質量%、Al_2O_3：３０～４５質量%、MgO：１２～１６質量%で、結晶相の主成分がコージェライトであることを特徴とする請求項１乃至４記載のセラミックハニカ

ムフィルタ。

【請求項６】　セラミック原料粉末に、平均粒径２０μm以上、粒径２０～１００μmが５０％以上の粒度分布を有する造孔材を少なくとも添加した後、水等を添加混合したバッチを、押出成形後、乾燥、焼成して得られるセラミックハニカム構造体の所定の流路端部を目封止し、該流路を区画する多孔質の隔壁に排気ガスを通過せしめることにより、排気ガス中に含まれる微粒子を除去するセラミックハニカムフィルタであって、前記多孔質隔壁表面及び多孔質隔壁内部に触媒が担持されているセラミックハニカムフィルタにおいて、前記多孔質隔壁は水銀圧入法により測定した場合に６０％以上の気孔率、１５μm以上の平均細孔径を有し、ｎ番目の測定点における細孔径に対する前記隔壁の累積細孔容積分布曲線の傾きS_nの最大値は０．７以上であり、前記累積細孔容積分布曲線の傾きS_nは下記式（１）

$$S_n=-(V_n-V_{n-1})/(\log(D_n)-\log(D_{n-1}))\quad(1)、$$

（但し、D_nは（ｎ）番目の測定点における細孔径（μm）であり、D_{n-1}は（ｎ－１）番目の測定点における細孔径（μm）であり、V_nは(ｎ)番目の測定点における累積細孔容積（cm^3／ｇ）であり、V_{n-1}は(ｎ－１)番目の測定点における累積細孔容積（cm^3／ｇ）である。）により表されることを特徴とするセラミックハニカムフィルタ。

【手続補正２】

【補正対象書類名】明細書

【補正対象項目名】０００７

【補正方法】変更

【補正内容】

【０００７】

【課題を解決するための手段】上記課題を解決するため、本発明者は鋭意検討を行った結果、ハニカム構造体の隔壁に形成される細孔の分布をある一定範囲内とすることにより、低圧力損失、高捕集効率、さらには高強度の３つの特性を満足させたセラミックハニカムフィルタが得られることを見出し、本発明に想到した。すなわち、本発明のセラミックハニカムフィルタは、セラミック原料粉末に、平均粒径２０μm以上、粒径２０～１００μmが５０％以上の粒度分布を有する造孔材、水等を添加混合したバッチを、押出成形後、乾燥、焼成して得られるセラミックハニカム構造体の所定の流路端部を目封止し、該流路を区画する多孔質の隔壁に排気ガスを通過せしめることにより、排気ガス中に含まれる微粒子を除去するセラミックハニカムフィルタにおいて、前記多孔質隔壁は水銀圧入法により測定した場合に６０％以上の気孔率、１５μm以上の平均細孔径を有し、前記多孔質隔壁の累積細孔容積分布曲線の傾きに関する下記式（１）

$$S_n=-(V_n-V_{n-1})/(\log(D_n)-\log(D_{n-1}))\quad(1)、$$

（但し、D_nは（ｎ）番目の測定点における細孔径（μm）であり、D_{n-1}は（ｎ－１）番目の測定点における細孔径（μm）であり、V_nは(ｎ)番目の測定点における累積細孔容積（cm^3／ｇ）であり、V_{n-1}は(ｎ－１)番目の測定点における累積細孔容積（cm^3／ｇ）であり、S_nはｎ番目の測定点における細孔径に対する累積細孔容積分布曲線の傾きである。）により表されるS_nの最大値が０．７以上であることを特徴とする。この時、S_nの最大値は０．９以上であることが好ましく、気孔率は６０～８０％、平均細孔径は１５～４０μmであることが好適である。さらに、隔壁を構成する多孔質セラミックスの主成分の化学組成がSiO_2：４２～５６質量％、Al_2O_3：３０～４５質量％、MgO：１２～１６質量％で、結晶相の主成分がコージェライトであることが好適である。また、本発明のセラミックハニカムフィルタは、セラミック原料粉末に、平均粒径２０μm以上、粒径２０～１００μmが５０％以上の粒度分布を有する造孔材、水等を添加混合したバッチを、押出成形後、乾燥、焼成して得られるセラミックハニカム構造体の所定の流路端部を目封止し、該流路を区画する多孔質の隔壁に排気ガスを通過せしめることにより、排気ガス中に含まれる微粒子を除去するセラミックハニカムフィルタであって、前記多孔質隔壁表面及び多孔質隔壁内部に触媒が担持されているセラミックハニカムフィルタにおいて、前記多孔質隔壁は水銀圧入法により測定した場合に６０％以上の気孔率、１５μm以上の平均細孔径を有し、前記多孔質隔壁の累積細孔容積分布曲線の傾きに関する下記式（１）

$$S_n=-(V_n-V_{n-1})/(\log(D_n)-\log(D_{n-1}))\quad(1)、$$

（但し、D_nは（ｎ）番目の測定点における細孔径（μm）であり、D_{n-1}は（ｎ－１）番目の測定点における細孔径（μm）であり、V_nは(ｎ)番目の測定点における累積細孔容積（cm^3／ｇ）であり、V_{n-1}は(ｎ－１)番目の測定点における累積細孔容積（cm^3／ｇ）であり、S_nはｎ番目の測定点における細孔径に対する累積細孔容積分布曲線の傾きである。）により表されるS_nの最大値が０．７以上であることを特徴とする。

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